THE GENERATION OF CO IN BENCH-SCALE FIRE TESTS AND THE PREDICTION FOR REAL-SCALE FIRES

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ABSTRACT

Carbon monoxide (CO) is the single most important factor associated with deaths in fires; thus, predictions of CO developed in fires is an essential aspect of fire quantification. It is considered crucial to have correct CO prediction methods for post-flashover fire stages, since, in the United States at least, the majority of fire deaths are associated with fires which have gone to flashover. In this paper, it is shown that the yields of CO observed in real-scale fires are generally not related to either the chemical nature of the material being burned nor to the yield observed for the same material in bench-scale testing. Instead, the generation of CO in real-scale fires is determined largely according to the oxygen available for combustion, with thermal conditions of the fire plume also playing a significant role. This behavior is in sharp contrast to many other material fire properties, including yields of gases such as CO_2 and HCl, which can be predicted for real-scale fires from bench-scale results. Finally, results from various studies completed thus far indicate how effective prediction of real-scale CO yields may be accomplished. While bench-scale measurements are not necessary to predict real-scale CO, bench-scale toxic potency measurements can be in error if the CO component in them does not reflect on the real-scale CO yield. Thus, a method is developed whereby the bench-scale toxic potency measurements can be computationally corrected to better approximate the toxic potencies measured in real-scale, post-flashover room fires. These techniques will, undoubtedly, be further refined as additional experimental results become available.

Keywords: carbon monoxide; Cone Calorimeter; fire hazard; fire toxicity; room fire tests; scaling.

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INTRODUCTION

High carboxyhemoglobin (COHb) in most fire victims indicates that CO inhalation is the primary cause of most fire deaths [1]. Thus, it is extremely important that CO should be treated correctly in both fire tests and in fire hazard analyses.

Conventional wisdom often states that CO levels (commonly expressed as CO/CO_2 ratios) are uniquely associated with the stages of a fire. For instance, the guidance document [2] published by the International Organization for Standardization (ISO) giving the inverse CO_2/CO ratios, states:

Stage of fire	CO_2/CO ratio
developing (flaming)	100 - 200
fully-developed (flaming) low ventilation	< 10
fully-developed (flaming) high ventilation	<100

These CO level guidelines were based primarily on a broad-brush distillation of various older studies. While carefully-done studies (e.g. [3]) can be cited, they typically lacked instrumentation, such as air flow rate measurements, which today we view as essential towards producing useful engineering data. Thus, over-generalized guidance such as was the best that ISO could offer, is not useful for hazard analysis; worse yet, it can be quite misleading.

One early indication of the need to analyze the CO production situation more carefully came from a study conducted in Japan [4]. In one portion of this carefully-controlled test series, the compartment size and the ventilation were kept constant. As the fuel burning rate was increased (and, therefore, the fuel/air ratio increased, due to the design of these experiments), however, the yield[2] of CO suddenly dropped!

Over the last few years, the issues associated with CO production have received intensive study. One milestone was a 1988 workshop designed to identify the state of the art in this area [5]. Since then, a number of additional research studies have been completed and some useful, albeit tentative, engineering guidance is available. In this paper we present some of the basic principles which are useful to understand CO production. The differences between CO production in full-scale fires (or fire tests) and in bench-scale tests are then explored. It is shown that, as a rough generalization, *all* bench-scale flammability or toxicity tests are likely to exhibit unrealistic CO levels. Finally, a computation method is offered whereby such bench-scale test data can be post-corrected in order to arrive at a reasonable representation of real-fire behavior.

[2] Concentrations of CO are often reported as the experimental result, but lack usefulness since this quantity is totally apparatus-dependent. The preference is to report the CO *yield*, which is defined as f_{CO} = mass CO produced/mass specimen lost.

CO IN REAL-SCALE FIRES

There have been a very large number of studies where CO production in real-scale fires is examined. We will not be reviewing the bulk of this literature here, since the majority of these studies lack generality and do not offer a means of providing useful, quantitative engineering guidance. By examining available data, however, the following conceptual framework can be outlined. It represents the best current understanding; this is generally similar to that given in [5, pp. 62-3].

- During the early stages of a room fire, the CO yield in the room fire depends a great deal on the chemistry of the fuel being burned. Yields of CO for a very small room fire will be similar to those seen in the Cone Calorimeter [6], the radiant toxicity test [7], or any number of other bench-scale fire tests. This is not surprising, since a very small room fire can be of the same scale as the burning specimen in the bench-scale test. For wood, the CO yield in this stage of burning can be about 0.002 g/g. For materials which are fire-retardant treated or are innately difficult to burn due to their chemical structure, this value will be much higher. (Note that this does *not* imply an increased fire hazard for such materials; indeed, generally the converse is the case, for reasons given in considerable detail in [8].)

- For greater burning rates in the room fire, as the fuel/air ratio increases, the CO yield tends to become independent of the chemical nature of the fuel being burned and dependent only on the 'global equivalence ratio,' which is defined as

$$\varphi = \frac{(kg\ fuel/kg\ air)}{(kg\ fuel/kg\ air)_{stoich}} \qquad (1)$$

  where 'stoich' denotes conditions at which the ratio between fuel and oxygen is in the amount required to yield complete combustion, with no excess oxygen and no excess fuel.

- As the fire size increases, the fuel/air ratio increases and the CO yield rises. This, however, is true only over a limited range of φ.

- In the later stages of the fire, there will often be a fire plume formed at the door or window. This door plume may be effective, ineffective, or partly effective in incinerating the CO coming from the fire room. If the plume is effectively incinerating, then very low values of CO yield can be seen downstream of this plume. If the plume is ineffective, then the downstream CO yield will not be appreciably different from that at the doorway.

- The plume is most likely to be effective in incinerating CO when it goes straight up, does not impinge on any physical obstacles, and is located in an area with plentiful oxygen. Conversely, effectiveness may be low if the plume is flattened horizontally against a ceiling, impinges on obstacles which are heat drains, or gets its air by pulling it from a long corridor rather than from the open atmosphere.

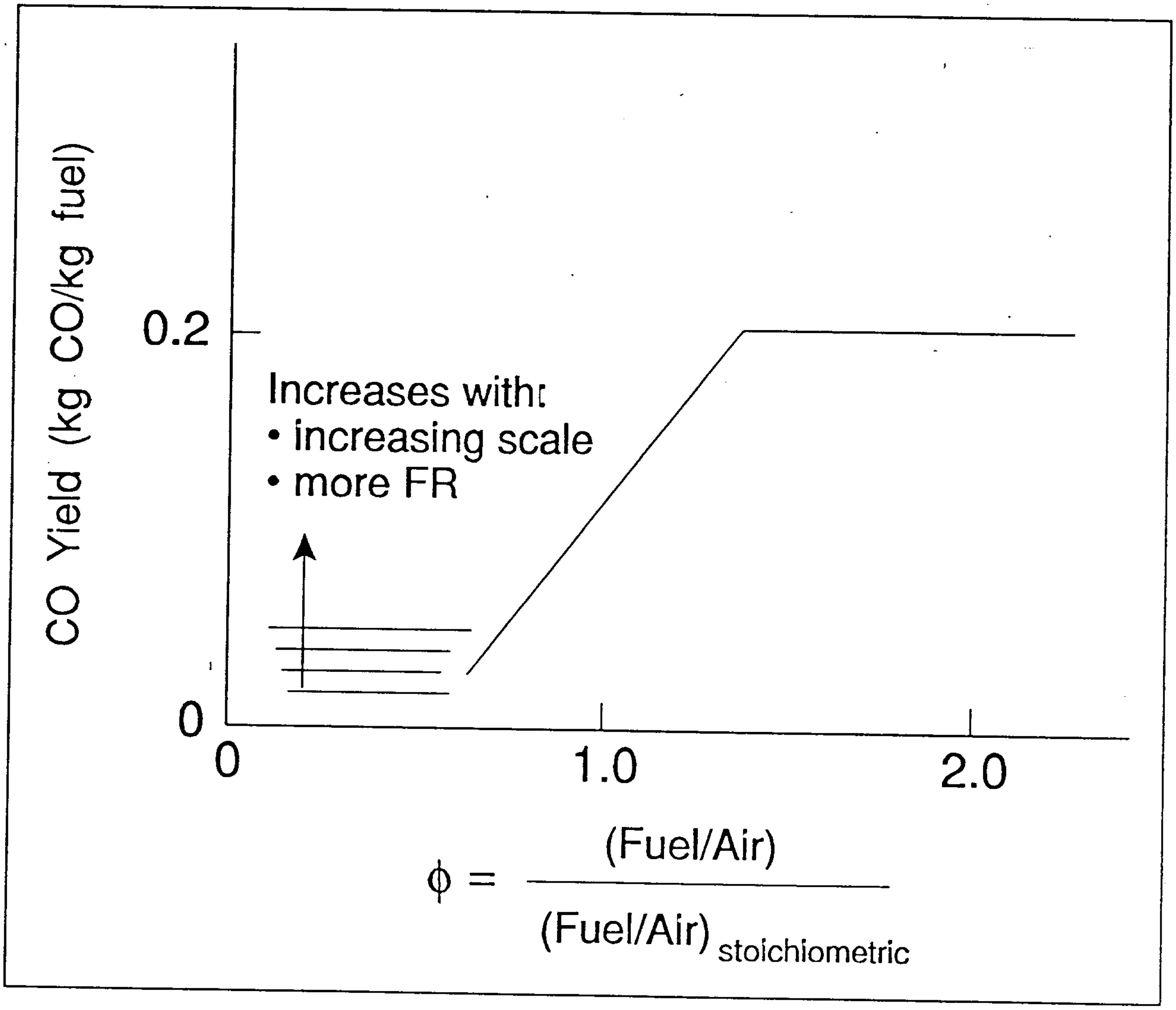

Figure 1 Schematic representation of variables affecting CO yields in real-scale fires.

- The same room fire may discharge gas streams with very different CO concentrations. One stream may, for example, pass through an effectively-incinerating plume, whereas another one may pass through heat-draining obstacles, or into a stagnant air volume, or otherwise not be incinerated.

Figure 1 represents schematically the conceptual model outlined above.

REAL-SCALE DATA

We will now turn to examine some of the quantitative data available upon which this generalized conceptual framework was constructed. Mulholland conducted an extensive examination of a number of real-scale fire tests conducted at NIST [9],[8],[10],[11] where adequate experimental techniques were used, where φ was successfully quantified, and reliable data were available [12]. Even with careful selection of tests to be used, he found a large amount of data scatter; nonetheless, it was possible to conclude that $f_{CO} \approx 0.2$ represented those post-flashover fires where plume incineration did not appear to be taking place. This value did not depend–to within the scatter of the data–on the type of fuel being burned. The room fire tests [10] where PMMA panels were burned applied on the walls of a standard, full-scale burn room [13] are especially important to note (Figure 2). In the test configuration, the room exhaust flowed into a large collection hood. The nearly-vertical doorway plume could freely entrain air from the surroundings and burn. As a consequence, the CO/CO_2 ratio monitored downstream *in the exhaust stack* shows a continued increase up to about the time of room flashover. Afterwards, the ratio dropped to about 0.02 even though the fire size has increased. By contrast, the CO/CO_2 ratio monitored *in the room* (not shown in the figure) did not drop after flashover occurred. This room test graphically demonstrates the effects of plume incineration and also more quantitatively confirms the Japanese results referred to above.

INTERMEDIATE-SCALE DATA

While truly real-scale data would, of course, be most convincing, strong reliance will, in practice, have to be placed on a number of reduced-scale studies. These studies are germane since, unlike in standard bench-scale fire tests, the burning environment created was considered to be similar in nature to an actual room. The early studies of this nature are due to Beyler [14], who measured gas yields in an open experimental arrangement that has been termed a 'catcher hood.' In such an arrangement, the fuel flow is created by an adjustable burner (or, alternatively, various burning solid or liquid commodities). The air+fuel flow rate is controlled by placing the burning apparatus below a hood through which the flow can be adjusted; this effectively controls the air inflow rate and the fuel/air ratio. Morehart, Zukoski, and Kubota [15] also conducted catcher hood studies, but using a slightly different geometry whereby the catcher hood had no direct exhaust at all, but merely the shape of an upside-down oil drum. A gas burner could be set a variable distance below it. By adjusting this distance, the amount of air entrained along with the fuel could be varied. The combustion products left the drum by overflowing at the sides. Despite some differences in test geometry, the results from the two sets of investigators were very similar. Figure 3 shows the CO yield results obtained, with the PMMA, polyethylene and pine data

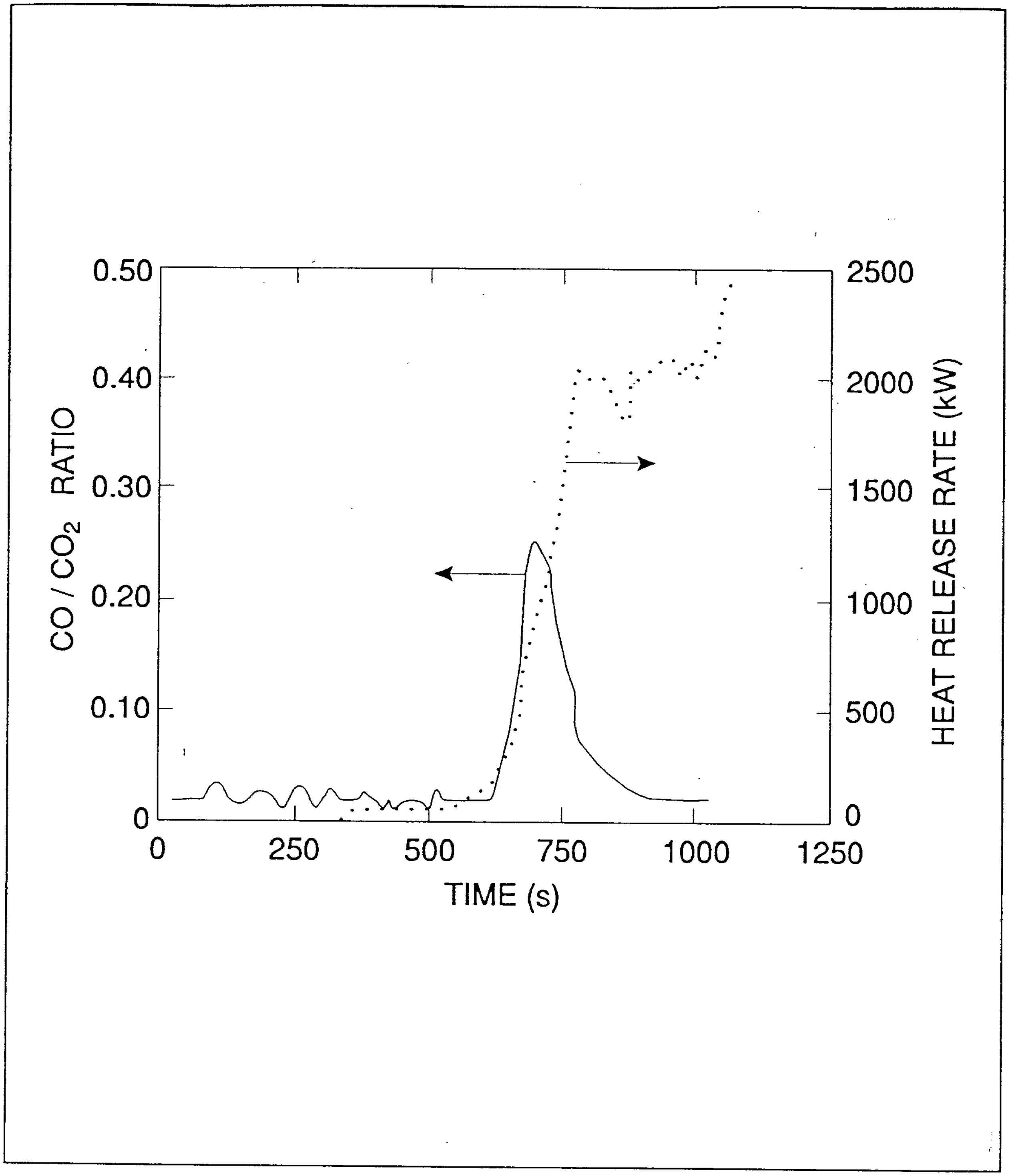

Figure 2 Results from a full-scale PMMA wall fire showing effective plume incineration of CO after flashover has occurred. The CO/CO_2 ratio was measured in the exhaust hood.

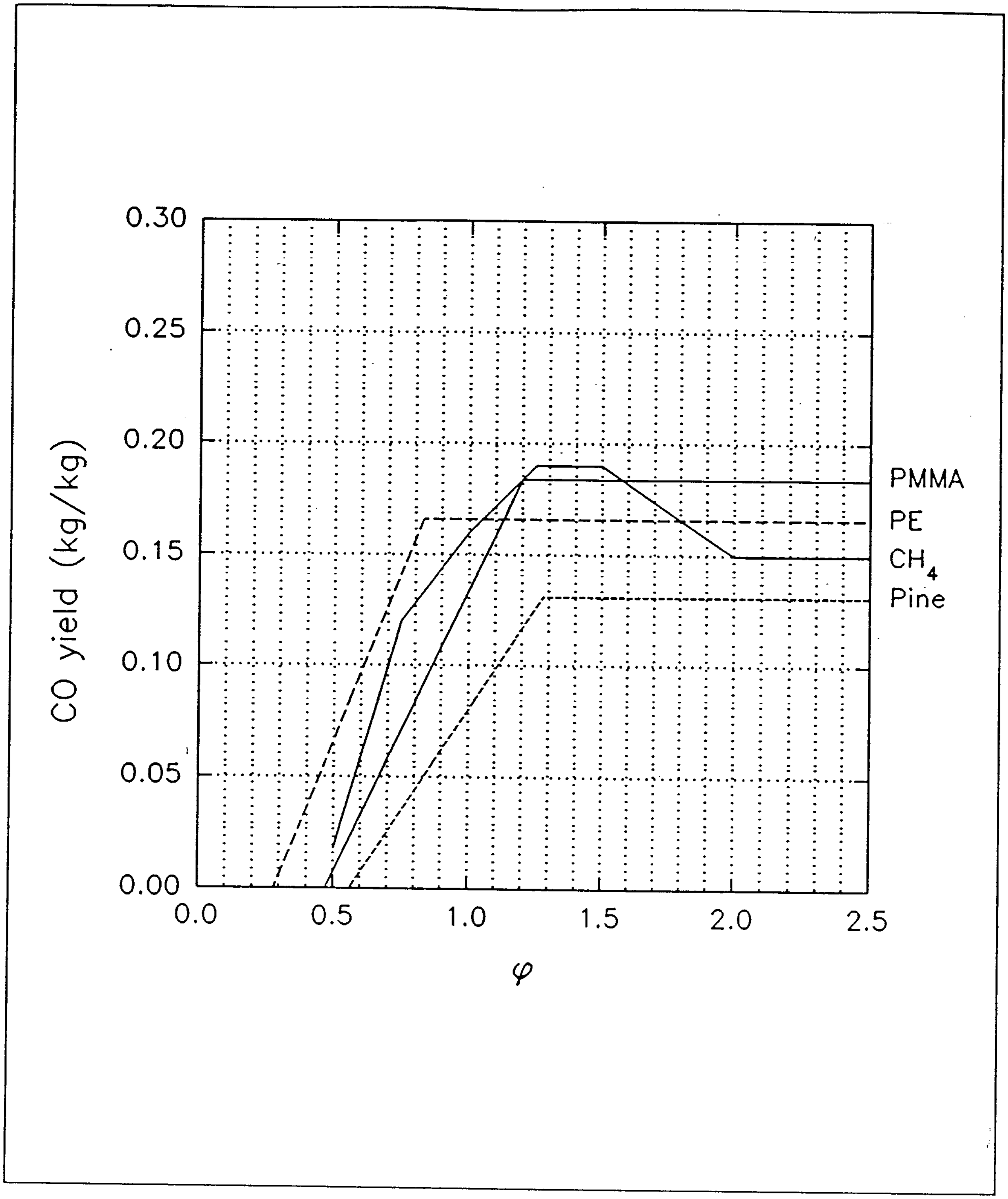

Figure 3 CO yields measured in catcher hood experiments, showing the (low temperature) data of Beyler and of Morehart *et al.*

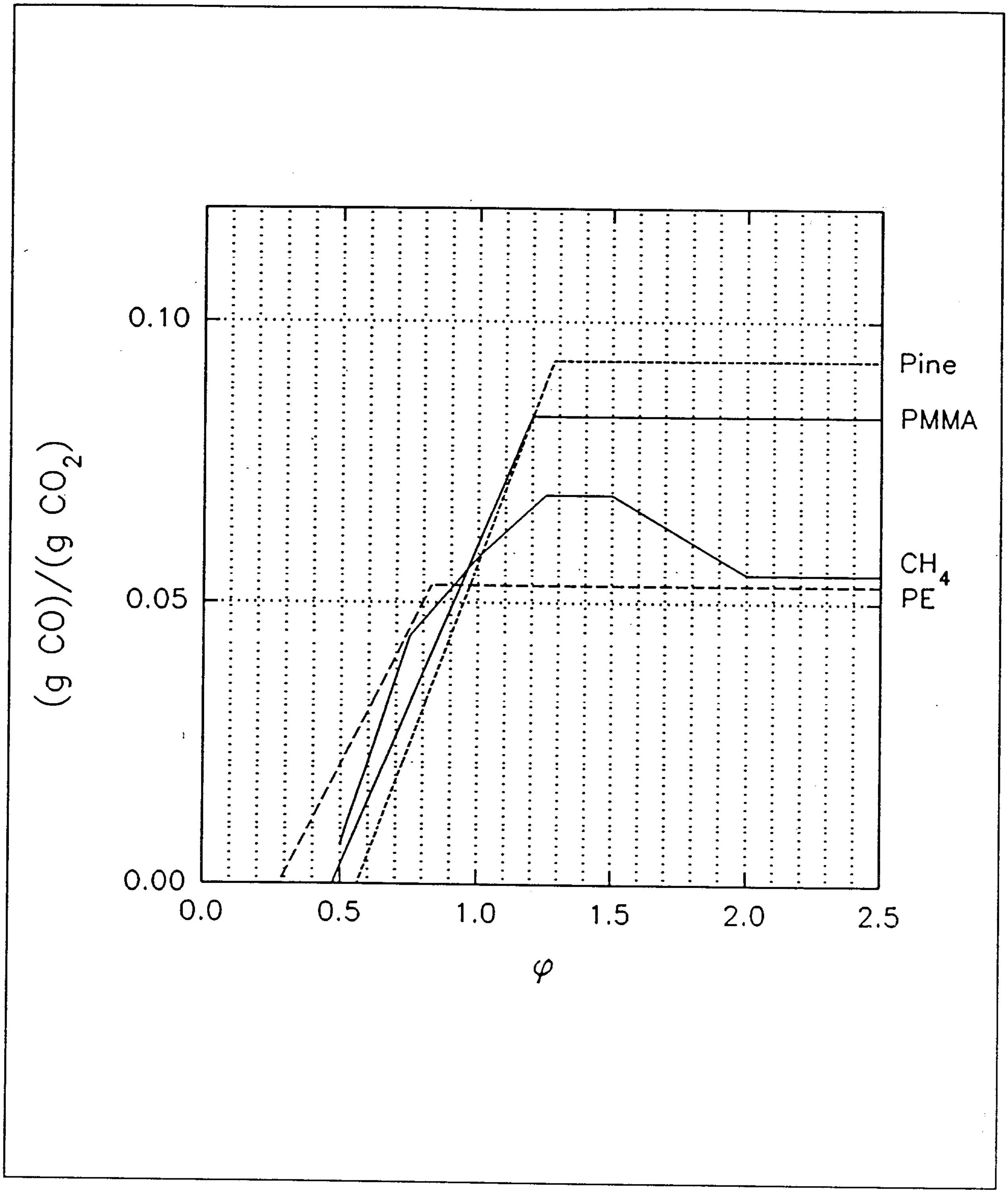

Figure 4 Results of the catcher hood experiments re-plotted as a CO/CO_2 mass ratio.

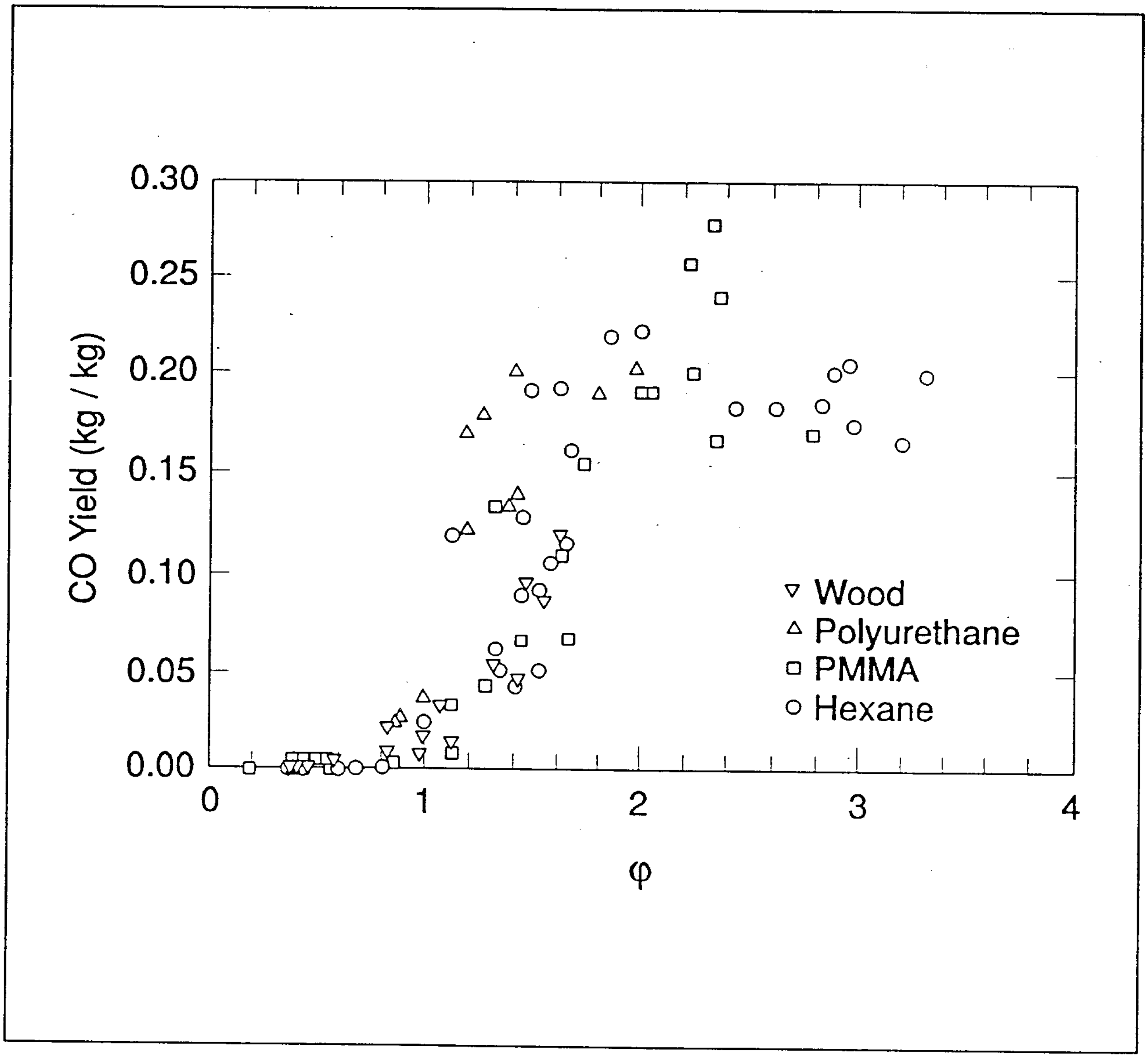

Figure 5 Results from tests by Roby and Beyler in an intermediate-scale enclosure with realistically high room temperatures

being from Beyler, while the methane data were from Morehart et al. The graphs have been somewhat simplified to portray only the major trends.

Figure 4 shows these data replotted in a slightly different variable, the CO/CO_2 ratio. This makes the rising portion of the curves fall on a single line, while differentiating two plateaus. The lower plateau, at $CO/CO_2 = 0.05$, corresponds to fuels which have no oxygen atoms in the fuel molecule. The higher plateau, at $CO/CO_2 = 0.08$, corresponds to oxygen-containing fuels.

The intermediate-scale results from both of the above experimental programs, while encouragingly similar, shared one similar drawback: unrealistically low temperatures. The temperatures of 460 - 870 K obtained in these catcher hood tests simply do not represent room fire temperatures in flashed-over fires, where $0.5 < \varphi < 2.5$. Such a range of fuel/air ratios would normally show temperatures of 1100 - 1300 K in a realistically configured real-scale room. Much higher temperatures could be achieved in a test rig recently constructed by Roby and Beyler [16]. This intermediate-scale rig resembles a standard fire test room, except that all the air inflow is supplied by an air duct through the floor, while the window opening represents only an outflow and no inflow. Temperatures in the vicinity of 1000 K could be achieved with this rig. The initial data of Roby and Beyler (Figure 5) [17] show trends almost identical to those in Figure 3 with one crucial difference: the x-axis is shifted, so that the intercept occurs at around $\varphi = 1.0$ instead of $\varphi = 0.5$. It is striking to note that the ultimate plateau for the Roby/Beyler data is at the same value of $f_{CO} \approx 0.2$ as was seen for the real-scale data by Mulholland. In a similar vein, Bryner [18] has been conducting experiments in a 2/5-scale model of the ASTM room; his results should be available in the near future and will provide additional numeric guidance.

Since the plateau values seen in Figure 3 for the intermediate-scale results are quite close to the $f_{CO} = 0.2$ observed in real-scale fires, it can be concluded that curves such as those in Figure 3 (except possibly shifted on the x-axis, as discussed above in conjunction with the newer measurement results) are also applicable to characterizing the real-scale fires.

THE BENCH-SCALE CO PROBLEM

In a previous comprehensive hazard analysis of fire-retardant-treated versus unretarded products [8] it was concluded that we cannot yet "predict accurately the production of CO from less-than-room-sized tests." The problem has not been solved in its entirety. Nonetheless, there is now available an empirical solution. We first outline the problem, then proceed to the needed solution.

By examining the data contained in the above-mentioned hazard study [8], in earlier studies on the fire toxicity of upholstered furniture [19],[20],[21], and in the recent toxicity validation study [22] certain general trends can be seen. The yields of certain combustion products (CO_2, HCl, HBr, HCN) are seen to be roughly independent of whether the measurement was taken in a closed-box bench-scale test (*e.g.*, the old cup furnace smoke toxicity method [23]; also the currently-used radiant toxicity test method [7]), a flow-through bench-scale test (*e.g.*, the Cone Calorimeter), an open burning environment (*e.g.*, the furniture calorimeter

[24]), or in an actual room fire. The number of combustion gases examined in this manner was not large, and some (for example, HCl) are difficult to measure to high precision. Nonetheless, the yields in the various scales and environments are similar, at least to the resolution of the measuring capability. This was emphatically not seen for one gas: CO. Table 1 shows the collected CO results.

Table 1 Yields of CO, as measured in various test programs (kg/kg fuel consumed).

Method	Test conditions	DF	RPU	PVC	NFR [a]	FR [b]	Chair NFR	Chair FR
Reference		[22]	[22]	[22]	[8]	[8]	[21]	[21]
Cup furnace	flaming	0.2	0.2	0.1	0.074	0.155	0.02	0.05
Radiant apparatus	50 kW/m^2	0.03 – 0.04	0.09 – 0.12	0.09	–	–	–	–
Cone Calorimeter	25 kW/m^2	–	–	–	–	–	0.01	0.05
	30 kW/m^2	–	–	–	0.02	0.06	–	–
	35 kW/m^2	0.005	0.06	0.08	–	–	–	–
	50 kW/m^2	0.003	0.08	0.08	–	–	–	–
	75 kW/m^2	0.003	0.04	0.07	–	–	–	–
Furniture Calorimeter	average	0.013	0.08	–	0.09	–	0.04	0.05
	steady-state	0.012	0.06	–	–	–	–	–
Real-scale	flaming	0.07 – 0.12	0.10 – 0.14	0.2 – 0.5	0.18	0.23	0.04 – 0.11	0.06 – 0.12

DF Douglas fir
RPU Rigid polyurethane foam
PVC Polyvinyl chloride
a Mixed commodities, all without fire retardants.
b Mixed commodities, all containing fire retardants.

The question can be asked whether this mis-match is caused by test irradiances used in bench-scale tests being different from those found in the real-scale fires. Table 1 shows some effects of the irradiance used in the bench-scale test, but some more explicit data can be seen in Figure 6. Cone Calorimeter results are shown there for two materials--Douglas fir and PMMA. For the thermoplastic material (PMMA) no effect of irradiance is seen. For the charring material (wood), however, a substantial decrease in f_{CO} with increasing irradiance is seen. At this time, sufficient data are not available to determine whether these trends are characteristic of such classes of materials or not. Paul [25] shows a similar independence for PMMA data, but the opposite behavior for cellulosics; his data, however, show a great deal of scatter and are reported only for lumped cellulosics, not an individual material.

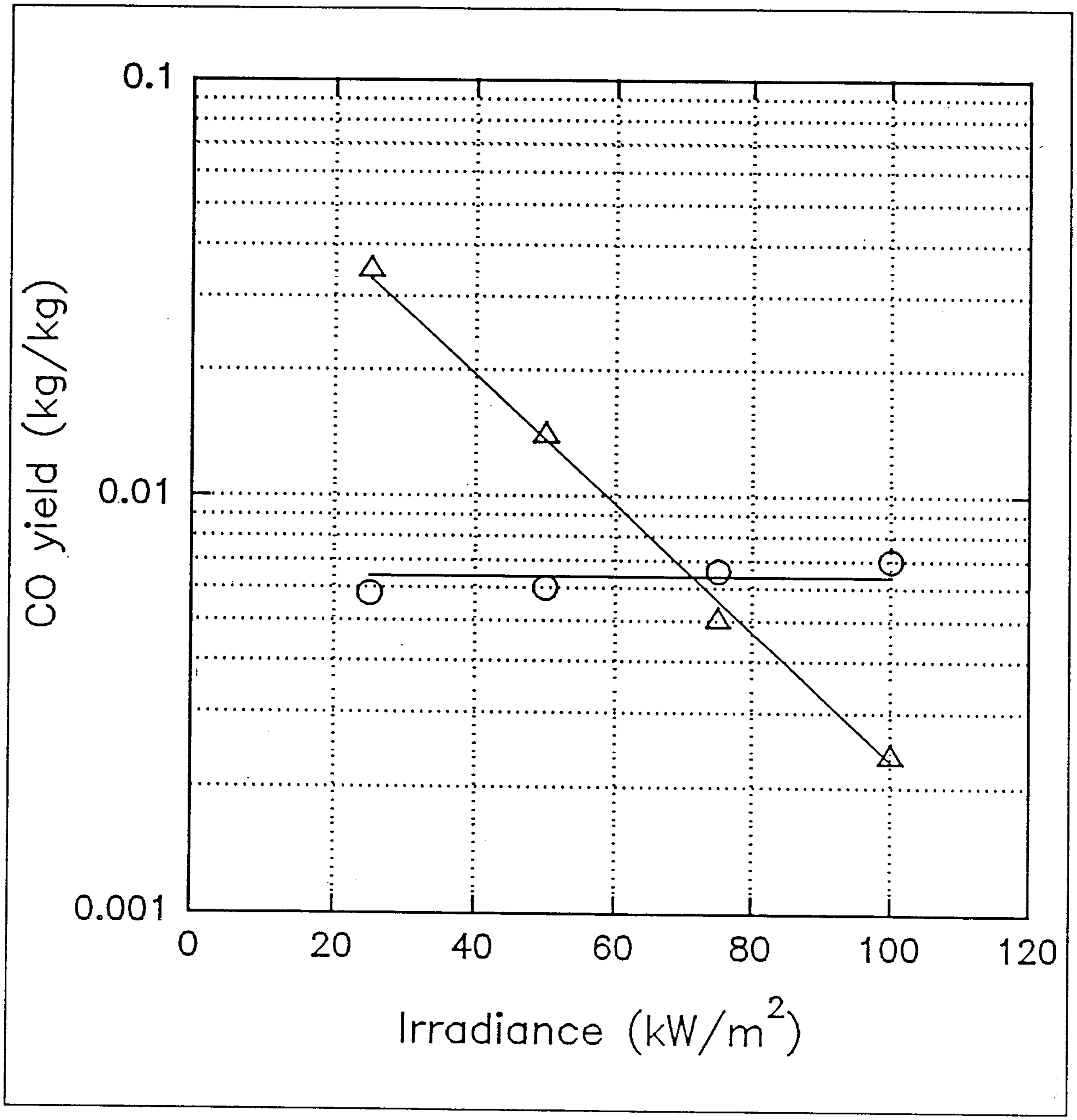

Figure 6 Comparison between CO yields measured in the Cone Calorimeter for a cellulosic material (Douglas fir, Δ) and a thermoplastic (PMMA, ○)

From the above results, it is clear that even if heat fluxes imposed on the specimen in the bench-scale test are similar to those in post-flashover fires, CO yields are not at all similar to those in such real-scale fires. The possible exception to this are products highly treated with fire retardants. Such products can show bench-scale yields in the vicinity of 0.2, but for different reasons. The simple solution would seem to be to lower the oxygen supply rate for the bench-scale test, yet this will be shown to be impractical.

DIFFERENCES BETWEEN CONDITIONS IN BENCH-SCALE TESTS AND IN REAL FIRES

To understand why the similarity of yields does not hold for CO, we must consider the details of the oxygen supply process during combustion. In general, there are two paths by which the supply of oxygen to the fire can be limited:

(1) By lowering the oxygen concentration in the incoming air stream from 21% to a lower value.

(2) By maintaining the oxygen concentration in the incoming air stream at 21%, but reducing the volume flow of air into the fire.

Control of CO by running a bench-scale test according to Path #1 is readily feasible and was recently examined by Mulholland and co-workers [26]. Their results are indicated in Figure 7. The left-most point for each fuel corresponds to the minimum oxygen concentration at which combustion can be sustained. It can be seen that this is, typically, about 13% to 14%. It can also be seen that there is a very regular dependence of the CO yield on the oxygen concentration. The important thing to note, however, is that the increase in CO, as one goes from a 21% air stream down to an air stream having 14% oxygen, is only by a factor of 2.5. Such CO yield values–which are the highest that can be seen in the Path #1 combustion–do not at all give bench-scale results similar to those seen in real-scale, post-flashover fires. Thus, running a bench-scale test according to Path #1 does not achieve the objective of generating bench-scale CO yields which can be used to represent the real-scale, post-flashover fire.

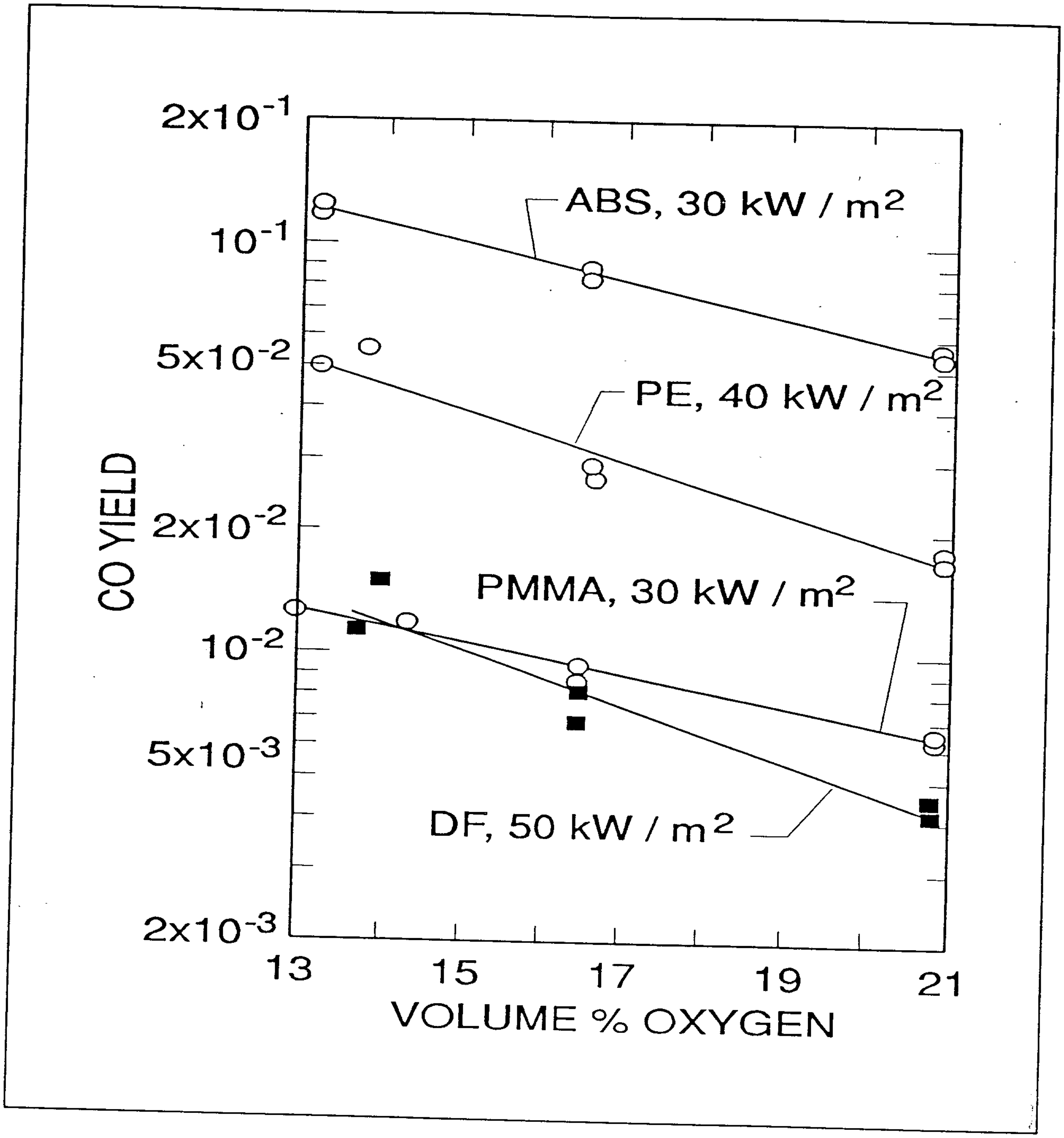

Figure 7 The dependence of CO yield (kg/kg fuel consumed) on oxygen concentration in the incoming air stream (ABS: acrylonitrile butadiene styrene; PE: polyethylene; PMMA: polymethylmethacrylate; DF: Douglas fir).

From the viewpoint of fire hazard, the CO increase associated with Path #2 is much more significant because it does represent what actually happens in a room fire. However, while Path #2 burning is feasible in a scaled-down model room experiment, as presented in the discussion of intermediate scale results above, such a testing paradigm is not practical for a bench-scale test. To simulate a fixed φ condition for a realistically-burning solid material sample would require not only the use of the room geometry, but also a continuously adjustable window opening. This is distinctly impractical.

More important, creating bench-scale test conditions to simulate the real-scale post-flashover CO yields is not **necessary**. The real-scale and intermediate-scale results available so far indicate that there is only a very small effect of fuel chemistry on the CO yield. Thus, conducting bench-scale tests on different products or materials to quantify a variable which hardly varies is not necessary.

If the full fire growth curve is desired to be modeled, then the low φ regime can be successfully represented by using data directly taken from the Cone Calorimeter or any other pertinent bench-scale test. In neither Figure 3 nor Figure 4 do we show data for low values of φ. This is because, in the regime where there is a copious amount of excess air, there is no dependence of CO on φ, there being, instead, another plateau [27]. The value of that low plateau (unlike the upper plateau) is highly dependent on fuel type.

Furthermore, the low-φ plateau appears to be also dependent on the scale of the combustion. Table 2 shows some detailed results from [8] on less-than-room-scale tests. It can be seen that for most products the larger-scale furniture calorimeter CO yields are higher than those in the bench-scale Cone Calorimeter. Also in most cases the FR item shows CO yields about a factor of 10 higher than the non-FR control (again, the *caveat* must be re-iterated that the **hazard** of the FR item is usually much lower than the control, due to decreased burning rate).

BENCH-SCALE TESTS FOR TOXIC POTENCY

Having stated that there is no need to measure CO in bench-scale tests if the objective is to estimate the f_{CO} in real-scale, post-flashover fires, it is important to realize that there are other important objectives for bench-scale tests. Since CO does not constitute the sole toxic fire gas of importance, tests for **toxic potency** may, in general, be required and they should certainly be no larger than bench-scale. If the CO levels created in such a bench-test are systematically different from those in real-scale, post-flashover fires, then serious errors can occur. Such errors can result in the bench-scale test results neither being able to predict the real-scale fire, nor even to rank products in their correct performance order. The latter would occur when comparing products with different amounts of FR agents or different ratios of CO to other-gas toxicity contributions.

Since the primary objective in such tests should be to represent post-flashover fires, matters would be simple if bench-scale test conditions could be created so that the sample is always burned at a fixed φ. As stated above, however, this is not possible. A recent study [7] has demonstrated that practical toxic potency measuring devices do not lend themselves to useful

Table 2 Additional details on CO yields for FR and non-FR materials, from [8].

Specimen	NFR /FR	CO (kg/kg)			CO_2 (kg/kg)		
		Cone Cal.	Furn. Cal.	Cup Furn.	Cone Cal.	Furn. Cal.	Cup Furn.
TV Cabinet H	NFR	0.015	0.12	0.084	2.28	1.39	2.09
TV Cabinet G	FR	0.109	0.37	0.18	0.67	0.74	0.78
Bus. Machine F	NFR	0.037	0.13	0.17	2.21	1.61	1.98
Bus. Machine A	FR	0.055	0.29	0.30	1.60	1.45	1.53
Chair T–whole	NFR	0.020	0.01	–	1.62	1.89	–
Chair S–whole	FR	0.051	–	–	0.964	–	–
Chair T–foam	NFR	0.016	–	0.025	1.71	–	2.05
Chair S–foam	FR	0.055	–	0.15	0.81	–	1.19
Cable D–whole	NFR	0.041	0.12	–	1.77	1.61	–
Cable K–whole	FR	0.060	0.10	–	1.34	1.04	–
Cable D–wire ins.	NFR	0.029	–	0.050	2.19	–	2.38
Cable K–wire ins.	FR	0.135	–	0.13	1.00	–	1.26
Circuit Bd. C	NFR	0.014	0.10	0.075	2.07	1.71	2.13
Circuit Bd. L	FR	0.103	0.10	0.15	1.87	1.36	1.24

Specimen	NFR /FR	HCN (kg/kg)			HBr (kg/kg)			HCl (kg/kg)		
		Cone Cal.	Furn. Cal.	Cup Furn.	Cone Cal	Furn. Cal.	Cup Furn.	Cone Cal.	Furn. Cal.	Cup Furn.
TV Cabinet H	NFR	–	–	–	–	–	–	–	–	–
TV Cabinet G	FR	–	–	–	0.069	0.082	0.017	–	–	–
Bus. Machine F	NFR	–	–	–	–	–	–	–	–	–
Bus. Machine A	FR	–	–	–	–	–	–	–	–	–
Chair T–whole	NFR	0.002	0.001	–	–	–	–	–	–	–
Chair S–whole	FR	0.005	–	–	–	–	–	0.023	–	–
Chair T–foam only	NFR	0.002	–	0.0007	–	–	–	–	–	–
Chair S–foam only	FR	0.0023	–	0.0032	–	–	–	0.022	–	–
Cable D–whole	NFR	–	–	–	–	–	–	0.112	0.121	–
Cable K–whole	FR	–	–	–	–	–	–	0.131	0.133	–
Cable D–wire ins.	NFR	–	–	–	–	–	–	ND	–	–
Cable K–wire ins.	FR	–	–	–	–	–	–	0.093	–	–
Circuit Bd. C	NFR	–	–	–	–	–	–	–	–	–
Circuit Bd. L	FR	–	–	–	0.022	–	0.0043	–	–	–

control of φ. Since it is not feasible to set φ to the desired value in a bench-scale test, how much of an error is being committed? The CO yields in the various bench-scale tests and even in the furniture calorimeter (Table 1) are up to an order of magnitude different from those in the corresponding room fires. It is especially important to note that such discrepancies are seen for the furniture calorimeter data, not just for the bench-scale test methods. The furniture calorimeter has been shown to be very useful in characterizing the heat release rate of a pre-flashover room fire [28]. Such a predictive relationship, however, does not hold true for post-flashover CO production. The furniture calorimeter is normally operated in the high excess air regime, with $\varphi \rightarrow 0$. The exact value of φ at which room flashover will be reached depends somewhat on the details of room construction. Nonetheless, for rooms roughly the size of the ASTM fire test room [29], flashover is reached generally at the time φ reaches a value of 0.5. Thus, it is not surprising that furniture calorimeter CO data, even though the commodities tested may be large in scale, do not represent the CO yields obtained in actual room fires.

ADJUSTING LC_{50}s FOR EXPECTED CO YIELD IN REAL-SCALE FIRES

Since it is not possible to design a bench-scale test to simulate the flashover conditions occurring in a room fire, it becomes important to establish an alternative means by which correct CO data could be utilized. We develop here an example based on the 200 L closed-box chamber represented by the radiant toxicity test method [7]; equations pertinent to other geometries can be readily derived from the same principles.

From [30] we take that the toxic fire hazard can be represented as proportional to an exposure dose, specifically, the Fractional Effective exposure Dose, FED, which for burning materials is computed as

$$FED = \frac{\dot{m}'' \times A}{\dot{V} \times LC_{50\,(c)}} \tag{2}$$

where

$\dot{m}''$ = specimen's mass loss rate ($kg \cdot s^{-1} \cdot m^{-2}$)
A = the area of specimen burning at any given time (m^2)
$\dot{V}$ = volume of air flow through room ($m^3 \cdot s^{-1}$)

and where we express the toxic potency as the LC_{50}, in SI units:

$$LC_{50\,(c)} = \left(\frac{kg}{m^3}\right) = \left(\frac{g}{l}\right) \tag{3}$$

We have written an explicit '(c)' to remind us that the units here are a concentration.

The toxicity data from gases, however, as opposed to burning solids, are usually expressed in (vol/vol), specifically (ppm) units. To convert to volume units,

$$LC_{50\,(v)} = \frac{29}{1.185}\,\frac{1000}{MW}\,LC_{50\,(c)} = \frac{24{,}500}{MW}\,LC_{50\,(c)} \tag{4}$$

where MW is the molecular weight of the gas in question.

It is easiest to express the gases being measured as yields, with f_x, being the yield of species x. When more than one toxic gas is being evolved, the FED equation becomes

$$FED = \frac{\dot{m}'' \times A}{\dot{V}} \sum_x \frac{f_x}{LC_{50-x\,(c)}} \tag{5}$$

Converting this to the appropriate form so we could use ppm units for LC_{50}'s, gives

$$FED = \frac{\dot{m}'' \times A}{\dot{V}} \sum_x \frac{f_x\, 24{,}500}{MW_x\, LC_{50-x\,(v)}} \tag{6}$$

Considering Eq. (2), above, we assume the material now has two components: that which is measured by animals in the LC_{50} determination, plus that due to the additional yield of CO which should have been induced in the bench-scale test apparatus, but was not.

Then,

$$FED = \frac{A}{\dot{V}}\left[\frac{\dot{m}''}{LC_{50}} + \frac{\dot{m}''_{\Delta CO}}{LC_{50-CO\,(c)}}\right] \tag{7}$$

Here, the $LC_{50\text{-}CO\,(c)}$ is the toxic potency of CO in units of ($kg \cdot m^{-3}$). The actual value of this $LC_{50\text{-}CO\,(c)}$ depends on the amount of CO_2 which is simultaneously present in the atmosphere. This effect is not a very sensitive function of the quantity of CO_2, and for this purpose it can be assumed that $LC_{50\text{-}CO\,(v)}$ = 4000 ppm for typical values of CO_2 being present [31]. This is equivalent to $LC_{50\text{-}CO\,(c)} = 4.58\ kg \cdot m^{-3}$.

The mass evolution rate of this CO-equivalent supplement term is:

$$\dot{m}''_{\Delta CO} = \dot{m}'' \times \Delta f_{CO} \tag{8}$$

where

$$\Delta f_{CO} = [\textit{required yield of CO}] - [\textit{measured yield of CO}] \tag{9}$$

For post-flashover fires, the real-scale $f_{CO} \equiv 0.2$ (kg/kg). Then,

$$FED = \frac{\dot{m}'' \times A}{\dot{V}} \left[\frac{1}{LC_{50}} + \frac{\Delta f_{CO}}{LC_{50\text{-}CO\ (c)}} \right] \tag{10}$$

$$\Delta f_{CO} = 0.2 - \frac{[CO]\ 0.200}{m_{100}} \times \frac{28}{24.5 \times 10^6} \tag{11}$$

where:
[CO] = avg. CO measured in chamber (ppm)
0.200 = volume of the 200 L chamber (m^3)
m_{100} = mass of specimen lost during test (kg)

Combining above, gives final answer:

$$FED = \frac{\dot{m}'' \times A}{\dot{V}} \left[\frac{1}{LC_{50}} + 44 - 5.0 \times 10^{-5} \frac{[CO]}{m_{100}} \right] \tag{12}$$

Note that the units of LC_{50} above are ($g \cdot \ell^{-1}$). Converting to common units, get:

$$FED = \frac{\dot{m}'' \times A}{\dot{V}} \left[\frac{10^3}{LC_{50}} + 44 - 5.0 \times 10^{-2} \frac{[CO]}{m_{100}} \right] \tag{13}$$

where the units are:
LC_{50} = ($g \cdot m^{-3}$)
[CO] = (ppm)
m_{100} = (g)

Finally, $\dot{V}$ is a property of the room geometry, not of the combustible being burned; it is not known when comparing products by themselves. Furthermore, the expression for A would involve constants which are, again, extraneous for comparing two different materials. Therefore, for comparing the relative performance of two or more combustibles, it is appropriate to derive a 'relative FED' by normalizing out $\dot{V}$ by setting it equal to 1.0. Also, an expression for the burning area, in the simplest analysis [30], puts $A \propto 1/t_{ig}$, where t_{ig} is the time to ignition (s), as measured in a bench-scale test[3].

$$relative\ \ FED = \frac{\dot{m}''}{t_{ig}} \left[\frac{10^3}{LC_{50}} + 44 - 5.0 \times 10^{-2} \frac{[CO]}{m_{100}} \right] \tag{14}$$

3 The derivation for this relationship is by no means self-evident; the reader is referred to details given in the above reference.

When the purpose of the obtaining the bench-scale toxic potency data is to represent the conditions of the post-flashover room fire, then the results can be expressed as a 'corrected LC_{50}.' From Eq. (9), get:

$$LC_{50}(corr) = \frac{1}{\dfrac{1}{LC_{50}} + \dfrac{\Delta f_{CO}}{LC_{50-CO\,(c)}}} \tag{15}$$

Giving,

$$LC_{50}(corr) = \frac{1}{\dfrac{1}{LC_{50}} + 44\times10^{-3} - 5.0\times 10^{-5}\dfrac{[CO]}{m_{100}}} \tag{16}$$

where the units of $LC_{50}(corr) = (g{\cdot}m^{-3})$

Since the equations developed above are mathematical manipulations of the FED equation, they are valid under all circumstances where the FED computational scheme is valid, even if the measured f_{CO} should be > 0.2, and, thus, the correction would decrease the toxicity of the specimen. Validity limits for the FED concept are further discussed in [7]. The recommendation is that the corrected LC_{50} value is the best representation of the toxic potency of products or materials burned in a post-flashover room fire. The validity of this recommendation has been demonstrated [7] by direct comparison against real-scale room fire test results. For pre-flashover fires, the procedure would be to use the raw LC_{50} value as measured in the bench-scale toxicity test without using the CO correction. Because of the smaller importance of pre-flashover deaths in the U.S. fire fatality picture, however, pre-flashover computations have not received extensive validation.

PROBLEMS REMAINING TO BE SOLVED

A viable engineering framework has been outlined, one which is consistent with the available data. Nonetheless, the available data are sparse, and significantly more work should still remain to be done. A more theoretically-based method would offer a more reliable basis for computation; work is ongoing in this direction [32], but results are not yet available for use. In the shorter term, in order to increase confidence with empirical engineering solutions, some items clearly are needed:

- Confirmatory real-scale (as opposed to intermediate-scale) f_{CO} studies. The present model, as summarized above, relies on fire temperature–within certain bounds–not being a significant factor on the CO yield. This aspect, especially, needs to be confirmed or revised.

- Further examination of a range of fuels, especially of widely differing chemical nature. While a small number of oxygenated and non-oxygenated hydrocarbon fuels have been explored so far, the list is not extensive. Fuels with various heteroatoms in their structure especially deserve investigation.

- The quantification of the plume incineration effect. It is reasonable to presume that this could be modeled by a concept of a freeze-out temperature, below which CO oxidation effectively stops. Thus, along the plume trajectory an energy balance would be used to account for the heat increase due to combustion reactions occurring (which are proportional to oxygen entrained) and losses which occur due to radiation, impingement against solid bodies acting as heat sinks, etc.

REFERENCES

[1] Birky, M.M., Halpin, B.M., Caplan, Y.H., Fisher, R.S., McAllister, J.M., and Dixon, A.M., Fire Fatality Study, *Fire and Materials*, 3, 211-217, 1979.

[2] Toxicity Testing of Fire Effluents – Part 1.: The State of the Art (ISO TR 9122-1). International Organization for Standardization, Geneva, 1990.

[3] Rasbash, D.J. and Stark, G.W.V., The Generation of Carbon Monoxide by Fires in Compartments (Fire Research Note No. 614). Fire Research Station, Borehamwood (1966).

[4] Saito, F., and Yoshida, M., Geometrical Effects for Combustion Behavior of Materials in Model Boxes, pp. 953-963 in *Proc. of the 8th Joint Panel Meeting UJNR Panel on Fire Research & Safety*, Building Research Institute, Tsukuba, Japan (1985).

[5] Pitts, W.M., Executive Summary for the Workshop on Developing a Predictive Capability for CO Formation in Fires (NISTIR 89-4093). [U.S.] Natl. Inst. Stand. and Tech. (1989).

[6] Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products using an Oxygen Consumption Calorimeter (E 1354). American Society for Testing and Materials, Philadelphia.

[7] Babrauskas, V., Levin, B.C., Gann, R.G., Paabo, M., Harris, R.H. jr., Peacock, R.D., and Yusa, S., Toxic Potency Measurement for Fire Hazard Analysis (Special Publication 827). Natl. Inst. Stand. and Technology, Gaithersburg (1991).

[8] Babrauskas, V., Harris, R.H., Jr., Gann, R.G., Levin, B.C., Lee, B.T., Peacock, R.D., Paabo, M., Twilley, W., Yoklavich, M.F., and Clark, H.M., Fire Hazard Comparison of Fire-Retarded and Non-Fire-Retarded Products (NBS Special Publication SP 749). [U.S.] Natl. Bur. Stand. (1988).

[9] Budnick, E.K., Mobile Home Fire Studies: Summary and Recommendations (NBSIR 79-1720), [U.S.] Natl. Bur. Stand. (1979).

[10] Lee, B.T., unpublished data on PMMA panel burns in ASTM room.

[11] Nelson, H.E., An Engineering Analysis of Fire Development in the Hospice of Southern Michigan, December 15, 1985, pp. 927-938 in *Fire Safety Science–Proc. of the 2nd Intl. Symp.*, Hemisphere Publ., New York (1989).

[12] Mulholland, G., private communication (1988).

[13] Proposed Standard Method for Room Fire Test of Wall and Ceiling Materials and Assemblies, *1982 Annual Book of ASTM Standards*, Part 18. American Society for Testing and Materials, Philadelphia (1982).

[14] Beyler, C.L., Major Species Production by Solid Fuels in a Two-Layer Compartment Fire Environment, pp. 431-440 in *Fire Safety Science–Proceedings of the First International Symposium*, C.E. Grant and P.J. Pagni, eds., Hemisphere Publ., Washington (1986).

[15] Morehart, J.H., Zukoski, E.E., and Kubota, T., Species Produced in Fires Burning in Two-Layered and Homogeneous Vitiated Environments (NIST-GCR-90-585). [U.S.] Natl. Inst. Stand. and Tech. (1990).

[16] Roby, R.J., and Beyler, C.L., Compartment Fire Combustion Dynamics (NIST-GCR-91-588). Natl. Inst. Standards and Technology (1991).

[17] Roby, R.J., and Beyler, C.L., Compartment Fire Combustion Dynamics (NIST/CFR Grant No. 60NANB8D0829), Final Report to NIST (1991); to be published.

[18] Bryner, N., unpublished results of studies made at NIST (1992).

[19] Braun, E., Levin, B.C., Paabo, M., Gurman, J., Holt, T., and Steel, J.S., Fire Toxicity Scaling (NBSIR 87-3510). [U.S.] Natl. Bur. Stand. (1987).

[20] Braun, E., Levin, B.C., Paabo, M., Gurman, J.L., Clark, H.M., and Yoklavich, M.F., Large-Scale Compartment Fire Toxicity Study: Comparison with Small-Scale Toxicity Test Results (NBSIR 88-3764). [U.S.] Natl. Bur. Stand. (1988).

[21] Braun, E., Gann, R.G., Levin, B.C., and Paabo, M., Combustion Product Toxic Potency Measurements: Comparison of a Small Scale Test and "Real-World" Fire, *J. Fire Sciences. 8*, 63-74 (1990).

[22] Babrauskas, V., Harris, R.H., Jr., Braun, E., Levin, B.C., Paabo, M., and Gann, R.G., The Role of Bench-Scale Test Data in Assessing Full-Scale Fire Toxicity (NIST Tech. Note 1284), [U.S.] Natl. Inst. Stand. and Tech. (1991).

[23] Levin, B.C., Fowell, A.J., Birky, M.M., Paabo, M., Stolte, A., and Malek, D., Further Development of a Test Method for the Assessment of the Acute Inhalation Toxicity of Combustion Products (NBSIR 82-2532). [U.S.] Natl. Bur. Stand. (1982).

[24] Upholstered Furniture: Burning Behaviour – Full Scale Test (NT FIRE 032). NORDTEST, Helsinki, Finland (1987).

[25] Paul, K.T., Letter to the Editor, *Fire Safety J. 18*, 203-204 (1992).

[26] Mulholland, G., Janssens, M., Yusa, S., and Babrauskas, V., The Effect of Oxygen Concentration on CO and Smoke Produced by Flames, submitted to *Fire Safety Science – Proc. of the Third International Symposium* (1991).

[27] Tewarson, A., Fully-Developed Enclosure Fires of Wood Cribs, pp. 1555-1566 in *20th Symp. (Intl.) on Combustion*, The Combustion Institute, Pittsburgh (1984).

[28] Babrauskas, V., Upholstered Furniture Room Fires – Measurements, Comparison With Furniture Calorimeter Data, and Flashover Predictions, *J. of Fire Sciences. 2*, 5-19 (1984).

[29] Proposed Standard Method for Room Fire Test of Wall and Ceiling Materials and Assemblies, *1982 Annual Book of ASTM Standards*, Part 18. American Society for Testing and Materials, Philadelphia (1982).

[30] Babrauskas, V., Toxic Hazard from Fires: A Simple Assessment Method, pp. 16.1 to 16.10 in *Fire: Control the Heat...Reduce the Hazard*, QMC Fire & Materials Centre, London (1988).

[31] Levin, B.C., data to be published.

[32] Pitts, W.M., Long-Range Plan for a Research Project on Carbon Monoxide Production and Prediction (NISTIR 89-4185). Natl. Inst. Standards and Technology (1989).